

# Photodegradation of a Ternary Iron(III)-Uranium(VI)-Citric Acid Complex

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*Scientists from Brookhaven National Laboratory have investigated how a mixture of compounds containing citric acid, iron, and uranium are degraded by light. Understanding the mechanisms involved in the photochemical degradation of metal-organic complexes should result in a process to treat uranium-containing waste streams while recovering the uranium.*

Citric acid [ $C_6H_8O_7$ ] is a naturally-occurring organic compound used to remove toxic metals and radionuclides from contaminated soils and sediments. It is easily dissolved in water and forms a variety of soluble complexes with metals. The nature of the metal-citrate complex formed depends upon the nature of the metal, the pH of the solution, and the stoichiometric ratio of metal to citric acid.

Biodegradation of the metal-citrate complexes by *Pseudomonas fluorescens* results in the production of carbon dioxide and water, and precipitation of the metal from the solution. In our laboratory, we have previously shown that the iron-citrate complex is readily biodegraded while the uranium-citrate complex is recalcitrant, but that, upon exposure to light, the uranium-citrate complex was photochemically degraded. When iron, uranium, and citric acid are present together, an iron-uranium-citrate complex is formed, which is also resistant to biodegradation.

To determine the mechanisms of light-induced degradation, or photodegradation, of iron-, uranium-, and iron-uranium-citrate complexes, we used extended x-ray absorption fine structure (EXAFS), with x-rays from beamline X11A at the NSLS. We established the molecular structure of each of the three complexes: iron-citrate, uranium-citrate and iron-uranium-citrate, and identified the nature of the metal precipitate formed following photodegradation.

The photodegradation mechanism for the complex depends upon its structure. The iron-citrate complex consists of a binuclear core containing two ferric [ $Fe^{3+}$ ] ions bound together by a bridging group made of a terminal carboxylate group of citric acid [ $C_5H_7O_5COO^-$ ] and an oxygen atom. Its photodegradation proceeds by a two-electron oxidation of citric acid to 3-oxoglutarate ( $C_5H_4O_5$ ) with reduction of ferric ions to ferrous [ $Fe^{2+}$ ] ions (**Figure 1A**). The ferrous ions are re-oxidized to ferric ions in the presence of photochemically generated hydrogen peroxide [ $H_2O_2$ ] and the iron precipitates as ferrihydrite [ $Fe(OH)_3$ ].

The uranium-citrate complex consists of a core of two uranium atoms bridged by hydroxyl groups (di- $\mu$ -OH bonding). In addition, attached to each uranium atom are three ligand groups from citric acid, which form a tridentate ring (chelate) to each uranyl ion [ $UO_2^{2+}$ ]. Uranium-citrate photodegradation proceeds by a two-electron transfer mechanism with the oxidation of citric acid to acetoacetic acid [ $C_4H_6O_3$ ] and the reduction of uranium to an insoluble tetravalent form (**Figure 1B**). The tetravalent uranium is subsequently re-oxidized to a hexavalent form by



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reacting with a photochemically-generated hydroperoxy radical  $\bullet\text{O}_2\text{H}$ , and the uranium precipitates from solution as schoepite  $[\text{UO}_3 \cdot 2\text{H}_2\text{O}]$ .

The ternary iron-uranium-citrate complex has a unique structure consisting of a citric acid molecule bound to a binuclear iron core similar to the iron-citrate complex, but the central carboxyl group  $[\text{COOH}]$  of each citric acid is bound to two uranyl ions. The remaining two citric acids form tridentate complexes with each uranyl ion. Photochemical degradation of the complex involves oxidation of citric acid and production of ferrous ions, similar to the iron-citrate complex (**Figure 1C**), but, in contrast to the uranium-citrate complex, no uranium reduction to the tetravalent form is observed. Iron and uranium precipitate as ferrihydrite and uranium hydroxide  $[\text{UO}_2(\text{OH})_2]$ , respectively.

These results show that the presence of iron affects not only the mechanism of photodegradation but also influences the nature, and thus the stability, of the precipitate formed.

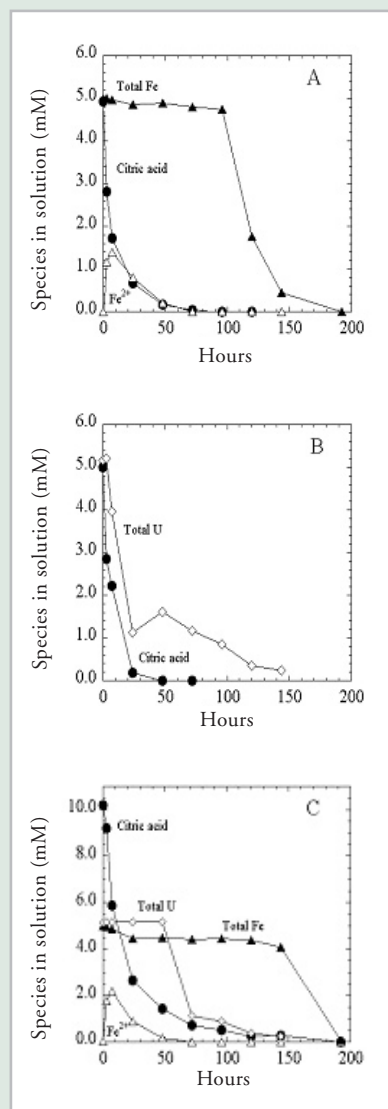


Figure 1. Organic metabolite production during photodegradation of: (A) 1:1 iron-citric acid, (B) 1:1 uranium-citric acid, and (C) 1:1:2 iron-uranium-citric acid complexes.